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CONDITIONS AFFECTING THE ACTIVITY OF IRON OXIDES IN REMOVING HYDROGEN SULPHIDE FROM CITY GAS

BY

W. A. DUNKLEY and R. D. LEITCH

This paper represents work done under a cooperative agreement between the Bureau of Mines, Department of the Interior, the State Geological Survey Division of the State of Illinois, and the Engineering Experiment Station of the University of Illinois

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SOME CONDITIONS AFFECTING THE ACTIVITY OF IRON OXIDES IN REMOVING HYDROGEN SULPHIDE FROM CITY GAS.

By W. A. Dunkley and R. D. Leitch.

PURPOSE OF INVESTIGATION.

The complete removal of hydrogen sulphide from city gas before distribution for domestic and industrial use is specifically required by law in nearly every State and municipality where public utility regulations are in force. Gas purification is therefore a subject of perennial interest to the gas industry. This interest is intensified by the fact that the purification methods now in general use limit the gas industry to the use of selected low-sulphur coals and oils for making gas. Iron oxide, the agent generally used for purifying gas, is often so variable in quality and uncertain in action that only by constant vigilance can the gas works at all times comply with the provisions of the law.

It has been recognized for several years that gas purification by the use of iron oxide is a more complex problem than it would appear to be at first. The fact that a particular material with a high iron oxide content may without apparent reason be inferior or even worthless for gas purification is evidence that iron oxide content alone is no criterion for judging the purifying value of a material.

Other chemical determinations, such as water content, have been suggested in conjunction with iron content as indices of oxide quality, but tests have shown that no general rule applies to all cases. It may be said, therefore, that our only guide to the purifying quality of an oxide is what the oxide will do when subjected to actual sulphiding, under conditions approximating those that obtain in practice.

TESTS OF IRON OXIDES.

Several tests have been devised for estimating the purifying value of iron oxides from the amount of hydrogen sulphide that they are capable of decomposing under certain prescribed conditions. In some tests the sulphiding of the oxide is brief and intensive, making necessary the use of pure hydrogen sulphide. In other tests the sulphiding is much slower, the content of hydrogen sul-

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phide being the same as in practical operation but the rate of gas flow much higher.

In either kind of test, factors causing uncertainty are introduced, but it is obviously impracticable to duplicate plant operation, wherein sulphiding with a single batch of material extends over months or even years under conditions that vary widely. A laboratory or semilaboratory test must be more or less intensive to permit its completion within a reasonable time, but it must be conducted in such a manner that, where conditions can not be controlled, their effects can at least be predicted. The purpose of this paper is to report the determined effects of some of these variable conditions upon the behavior of oxides used in purifying gas.

ACKNOWLEDGMENTS.

The experiments reported herein were made in the laboratories of the University of Illinois, where the equipment was furnished under a cooperative agreement entered into by the United States Bureau of Mines, the engineering experiment station of the university, and the Illinois State Geological Survey. Thanks are due to the various members of the 1922 purification committee of the American Gas Association for their work in checking the oxide testing method, herein described, with standard samples of oxide. Thanks are also due to Messrs. Fieldner, Powell, and Scott, of the Pittsburgh station of the Bureau of Mines, for devising the method in its first form. Several companies that produce gas oxide, including the Pennsylvania Salt Co., H. C. Frick Coke Co., Standard Silicon Co., Eph Lyon, E. J. Lavino & Co., Alpha-Lux Co., American Mineral Products & Coke Co., and Iron Oxide Products Co., cooperated by furnishing generous samples of their materials for the tests.

CHARACTERISTICS AFFECTING THE VALUE OF IRON OXIDES FOR PURIFYING GAS.

The ultimate criterion of oxide quality is what it will do in practice. That oxide is most valuable which, under the conditions prevailing in a given plant, will remove, at the lowest unit cost, the largest total amount of hydrogen sulphide from gas, and, if properly used, will always insure that the gas complies with regulations governing purity.

To meet these specifications, a material, in addition to being reasonable in price, must exhibit to a considerable degree these characteristics:

1. It must be active—that is, it must have the ability, as long as chemically active oxide remains in it, to react rapidly and completely with hydrogen sulphide.

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2. It must have capacity. It must contain enough active oxide to decompose a fairly large amount of hydrogen sulphide between revivifications, to avoid an excessive number of valve or box changes.

3. It must revivify completely and within a reasonable time when, after sulphiding, it is exposed to the air, either out of the purifier or in place.

If it is handled properly and is not spoiled with tar, an oxide that combines the above characteristics will be able to decompose a large amount of hydrogen sulphide before being finally discarded, and the spent material will show a high sulphur content.

Although it has long been recognized that the ultimate value of a purifying oxide depends on these innate characteristics, yet ideas on the definition and measurement of activity, capacity, and revivability have been rather vague. A plant operator may fill a purifying box with an oxide containing by analysis as much as 80 per cent of iron oxide. When the box is put into service it may perhaps remove the last traces of hydrogen sulphide for a few days; then an increasing proportion of hydrogen sulphide will begin to pass by the oxide. Analyzing the material when hydrogen sulphide begins to pass by it will usually show that only a small part of the iron oxide present has been sulphided. Another material may contain at the start less than half as much iron oxide and yet if used under practically the same conditions may completely purify gas of the same sulphur content for several weeks. This illustration is not meant to convey the idea that a material low in iron oxide is always superior to a material high in oxide, but such is sometimes the case. Evidently where two materials behave as described there must be some inherent difference between them. One is obviously more active chemically than the other. Similar differences appear in revivification.

Although the observed facts clearly point to such differences in oxides themselves, the reasons for the differences in behaviors are not clear and methods of comparison on a laboratory scale are not simple. To measure the activity of an oxide, it is necessary to define this property in numerical terms and then work out a test whereby numerical values can actually be obtained. The same is true of capacity and revivability. To work out and apply tests to the measurement of all three characteristics has not been feasible as yet. This paper deals chiefly with the property of activity, the conditions affecting it, and its approximate effect on the general value of a material.

MEASUREMENT OF OXIDE ACTIVITY.

Oxide activity may be defined as the rate of chemical reaction between hydrogen sulphide and iron oxide. As a reaction rate its measurement would seem possible either by the amount of hydrogen

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sulphide that could be decomposed in a unit time by a unit weight of the oxide, or by the rate at which an inert gas containing a definite amount of hydrogen sulphide could be passed through a definite weight of oxide with complete decomposition of the hydrogen sulphide by the oxide. The choice of method must take into consideration the mechanical difficulties involved, the possibility of unexpected effects of conditions not easily controlled, and the extent to which the method simulates commercial practice. In a paper written [1] in 1920 by one of the authors of this report, a method for determining oxide activity was described. The activity was measured in terms of the weight of pure dry H_2S that would be decomposed by 1 gram of the test material in one minute, per gram of actual Fe_2O_3 contained in the material—an excess of H_2S being in contact with the test sample throughout that time. The results obtained showed marked differences between various commercial materials. While these results seemed quite consistent and could be duplicated, there were some possible sources of error that could be questioned.

The sulphiding reaction is exothermic. With the liberation of the heat of the reaction in as short a time as one minute, to remove heat as rapidly as it is evolved is impracticable and consequently the temperature sometimes rises very rapidly. Since temperature decidedly affects the rapidity of many chemical reactions, the evolution of heat, even during the short duration of the test, might directly or indirectly affect results.

Concentration of H_2S is another factor to be considered because all the samples might not exhibit the same behavior with concentrated as with diluted H_2S. Even during the short period of one minute, some oxides decompose 85 to 90 per cent of their theoretical capacity for H_2S and therefore the rate of reaction may be affected by the constantly increasing content of the reaction products. In view of these uncertainties, it was deemed advisable to work out a test which would eliminate these variables or at least make them controllable. Such a test was suggested by members of the American Gas Association at a meeting in 1921, and a method [2] was subsequently devised by Messrs. Feldner, Powell, Scott, and other members of the United States Bureau of Mines Pittsburgh Station. Further improvements, which tend to facilitate manipulation, were added by the writers of this paper. The purpose of the test is to get a practically instantaneous value for oxide activity by determining the maximum rate at which an inert gas containing a low concentra-

[1] Dunkley, Wm. A., Some conditions affecting the usefulness of iron oxide for city gas purification: Engineering Experiment Station, University of Illinois, Bull. 119, 1921. 62 pp.

[2] Fieldner, A. C., Powell, A. R., and Scott, W., Determination of activity of oxides by rate of flow: Proc. Am. Gas Assoc., vol. 3, 1921, technical section, pp. 209–213.

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tion of hydrogen sulphide can be passed through a unit weight of material with complete removal of hydrogen sulphide. The rate of flow is measured in terms of cubic feet of gas per hour.

APPARATUS FOR TESTING ACTIVITY.

Figure 1 shows the arrangement of the apparatus described.

Two 12-liter aspirator bottles, *a* and *b*, are connected by ¾-inch rubber tubing. In bottle *a*, a mixture of hydrogen sulphide and illuminating gas is stored over water on which floats a layer of paraffin oil, *d*, to keep the water from absorbing the hydrogen sulphide. The leveling bottle *b* sits on a high stand or is suspended by a cord over a pulley so that it can be raised or lowered to regulate the level of the water. The flow of water from *b* to *a* is controlled by the ¾-inch lever-handle iron cock *j*. The gas storage space in bottle *a* is connected with a mercury manometer, *u*, for indicating gas pressure in the bottle at any time. From *a* the gas mixture passes through the three-way cock *v*, through the side outlet of which any excess pressure in *a* can be relieved; thence the mixture passes to the oxide tube *e* and to the indicator tube *f*—a test tube 1 inch in diameter containing 10 c. c. of a 5 per cent solution of lead acetate. The inlet tube dips into this solution about ½ inch. From the indicator tube the gas passes through the calibrated flow meter *g*, consisting of a short piece of capillary tubing with its ends connected to a water manometer tube, *h*, having a range of about 22 inches of water pressure. By means of the spring clamp *k* on the short piece of rubber tubing, the manometer can be shut off instantly and the reading held at any desired point.

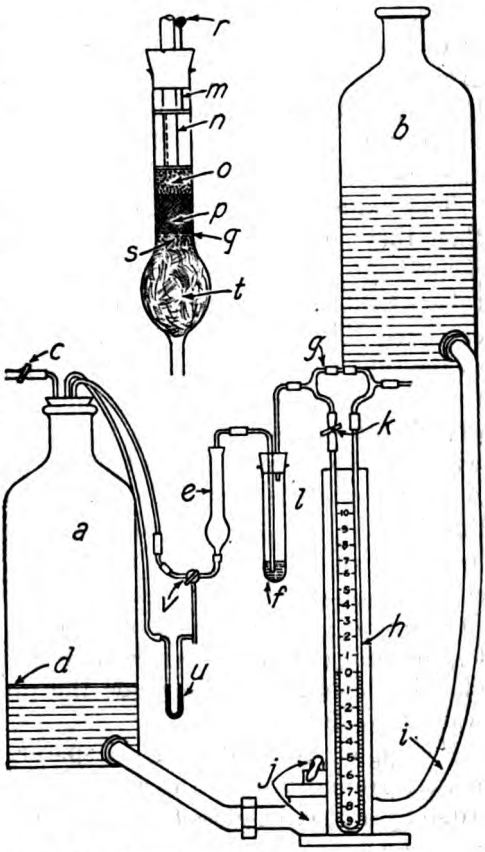

FIGURE 1.—Apparatus for determining the activity of oxides. For description, see text.

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PREPARATION FOR TESTING.

To obtain consistent results a few details of the preparation and operation of the apparatus should receive careful attention. Perhaps the most important detail is the placing of the oxide in the sample tube *e*. This tube, the straight portion of which is ⅝ inch in diameter and about 4 inches long, contains calcium chloride; the bulb *t* of the tube is filled with glass wool, on which is a layer, *s*, of clean white sand about ½ inch thick. The sand is fine enough to pass through a 20-mesh sieve but over a 28-mesh sieve. On the surface of the sand is a porcelain filter plate, *q*, the edge of which had been ground, on an emery wheel, until the plate fitted snugly in the tube. Resting on the filter plate is a mixture, *p*, of 1 gram of the oxide with ½ gram of air-dried sawdust that has been screened through a 20-mesh and over a 28-mesh sieve.

The oxides tested are ground to pass through a 20-mesh sieve: then they and the sawdust are mixed with a small spatula and poured into the tube *e* from a small scoop. While being filled the tube is held in a vertical position and rotated slowly around its vertical axis. The oxide-sawdust mixture is dropped around the wall of the tube because in this way the mixture can be placed in the tube much more uniformly. If the mixture is dropped down the center of the tube larger particles have a tendency to go to the outside with the result that the gas tends to pass along the wall of the tube. After the oxide is in the tube, the upper surface is leveled by tapping lightly, and over it is poured a thin layer, *o*, of sawdust whose thickness varies slightly, because it must be enough to make up the difference in volume between dense and light oxides and thus bring the surface always to a fixed level in the tube. Over this sawdust is poured 6 grams of sand, which is measured for each determination by a small closed-bottom glass tube made the proper size to hold that weight when level full.

Resting on the sand layer is a spacer, *n*, made of two porcelain filter plates, ground around the edges to fit loosely in the tube and separated by a piece of glass tube about 1¼ inches long but held together with a piece of fine copper wire. This spacer must be lowered to the surface of the sand with great care to avoid compressing the oxide. As compared with the deep sand layer used in the original apparatus, the spacer has the advantages that the weight on the oxide is always the same, there is less resistance to the flow of gas through the tube, and there is no tendency for the sand to be carried over into the indicator tube *f* by the rapid flow of gas necessary with very active oxides. The spacer is so dimensioned that it leaves only about ⅜ inch of free space, *m*, in the tube. A small hatpin, *r*, projecting through the rubber stopper is easily adjusted to serve as a

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stop, being forced through the stopper until it just touches the spacer without pressure. By following the directions as described, it is possible to secure very uniform conditions of packing.

Considerable experimenting with various solutions giving insoluble sulphides with H_2S resulted in a choice of a 5 per cent solution of lead acetate as the most sensitive for use with gas containing 300 or more grains of H_2S per 100 cubic feet. With very dilute H_2S mixtures even the lead acetate solution was not sensitive enough. For these concentrations a very dilute solution of potassium permanganate which showed only a faint purple color was used. A solution of satisfactory concentration was made up by adding 6 drops of normal potassium permanganate to 360 c. c. of distilled water. The decolorization of the solution was the end point when the permanganate was used.

TESTING PROCEDURE.

The testing procedure with the apparatus is as follows: The bottle *a* is filled with water on the surface of which is a layer of paraffin oil. Illuminating gas, bubbled through a solution of alkaline pyrogallate (if necessary) to remove oxygen, is then passed into the bottle until it is nearly full. While bottle *a* is being filled, bottle *b* is lowered until the mercury manometer *u* shows atmospheric or slightly greater than atmospheric pressure in *a*. When bottle *a* is nearly full of gas, a measured volume of pure H_2S is introduced from a gas burette; in practice the amount introduced will depend upon the concentration of gas to be purified. Experiments have shown that H_2S concentration affects oxide activity, but most oxides are affected similarly. After the gas mixture in bottle *a* has stood at least one-half hour to insure diffusion, the testing can be started. Oxide tube *e* is put in place. The operator opens the spring clamp *k* and holds it open with his right hand; then he opens the lever-handle cock *j* rather rapidly with his left hand while he carefully watches the indicator tube. As soon as there is the faintest indication of blackening in the lead acetate solution or of decolorizing, if permanganate solution is used, the spring clamp *k* is allowed to close, thus holding the water in the manometer at the instantaneous level corresponding to the rate of flow at the time when a trace of H_2S began to pass by the oxide tube.

At first some practice is necessary to determine how much the lever-handle cock must be opened to get the proper rate of gas flow through the oxide; the degree of opening varies somewhat with the difference in the water levels of bottles *a* and *b*. In order to determine approximately the opening necessary to allow the minimum rate of gas flow necessary to give the end point almost instantly without the proper rate being exceeded, it is advisable to make a

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preliminary run with each oxide tested, the cock *j* being opened rather gradually. When the proper opening has been determined, the gas flow can be brought up to the indicated rate almost instantly on subsequent trials with fresh portions of the same oxide and a fresh indicator. The rate at which gas bubbles through the indicator solution in tube *f*, when the proper rate is approximated, is also a guide to the practiced eye. It is important to get as nearly as possible the instantaneous value for the gas rate that just permits a trace of H_2S to pass the oxide tube, because, if the rate is increased too gradually, partial sulphiding diminishes the activity of the oxide before its true activity can be determined. Experiments made with the apparatus show that after a little practice an operator can check determinations very closely, even though the manometer tube is covered so that he can not see it.

The flow meter is a very simple device consisting of a piece of capillary tubing about 1 inch long. The water manometer indicates the difference in pressure between the inlet and outlet of this tube. It is convenient to calibrate two or three tubes of different bores by connecting the tube to be calibrated in series with a gas meter and, by the aid of a stop watch, determining the rate of gas flow in cubic feet per hour corrected, corresponding to various differential pressure readings. Where the house gas line will not give pressure enough for the higher rates of flow, these pressures may be obtained by filling the bottle *a* with gas and connecting its outlet directly to the flow meter, which is ahead of the gas meter.

With the apparatus just described and the procedure outlined, the rate of gas flow corresponding to the activity of a given oxide sample can be checked within two or three tenths of an inch—a difference corresponding to perhaps 0.25 cubic feet per hour.

The method apparently has several advantages over other methods that have been suggested. The value obtained is practically instantaneous and is not vitiated by the capacity effect which results when a material is rendered less active by sulphiding for a considerable period of time. The percentage of H_2S actually decomposed is so small that very little heat is evolved and that is carried away at once by the gas current; therefore this factor, which plays an important part in the rate of most chemical reactions, can apparently be neglected without introducing any appreciable error. Further, the rate of flow method simulates more nearly than other laboratory methods the conditions existing in practice, where gas of a comparatively low H_2S content is passed rapidly through the oxide layer.

CONDITIONS AFFECTING OXIDE ACTIVITY.

The activity of iron oxides in reacting with hydrogen sulphide is presumably affected by certain conditions. Some of these effects are

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known in a general way; others, judged from the literature available, seem to have been little studied. Among the variable conditions affecting oxide activity are water content of the oxide, concentration of H_2S in the gas being purified, temperature of the oxide, pressure of the gas, changed condition of the oxide after revivification one or more times, effect of tar and oil vapors in the gas, effect of acidity or alkalinity of the oxide, the influence of other chemical substances acting as promoters or catalyzers of the sulphiding and revivifying reactions, and, most important of all perhaps, the physical structure and surface condition of the oxide. As several variable conditions may exercise their effects simultaneously in the same or in opposite directions, it is important in studying one variable, either to eliminate all other variables or to determine the nature and extent of the effects of those that can not be eliminated. The authors of this report have sought to accomplish this as far as possible.

OXIDES TESTED.

It was desired to study the effects of these various conditions on oxides representing all the types commonly marketed for purification purposes. A number of oxide producers kindly submitted samples of their materials, which in this paper are identified by number only. As, however, the oxides represent certain types, they may be described under the following classification:

Samples 1 and 7: These materials were much alike, both physically and chemically, and were almost black. No. 1 is said to be a by-product of the dye industry. No. 7 is said to be made from iron borings by a secret rusting process; its physical appearance is much different from that of most oxides made by the rusting process. Both Nos. 1 and 7 contained between 3 and 4 per cent of free iron; both were attracted by a magnet. Examination showed that both samples consisted chiefly of the magnetic oxide of iron (Fe_3O_4); the iron content of each sample was very high.

Sample No. 2 was a natural oxide of iron, as shown by the presence of small rootlets. It was finely divided and its color was yellowish brown.

Sample No. 3 was a rusted-borings oxide; it looked like oxides usually made by that process, and was light brown in color.

Sample 4 was deep red. It was perhaps a pyritic cinder of uncertain origin.

Sample 5 had been made artificially by precipitation of a very dilute iron sulphate solution with finely ground calcium carbonate. Its color was yellowish brown.

Samples 6 and 8 were also precipitated oxides, by-products of the aluminum industry. No. 6 was much lighter colored than No 8 which was distinctly reddish.

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Table 1 gives analytical data on these samples:

TABLE 1.—*Analyses of oxides tested, air-dried basis.*

Sample No.	1	2	3	4	5	6	7	8
Fe_2O_3		51.80	79.85	72.67	24.20	42.39		51.75
Fe_3O_4	81.50						85.50	
Fe	3.76	0.79	0.46	0.51	1.02	1.96	3.23	
Al_2O_3	0.50	1.00		1.83	13.97	13.84		10.55
$CaCO_3$	0.34	1.91			23.32	7.00		
$CaSO_4$				1.17	1.40			
CaO	0.16	3.92			7.18	7.13		
SiO_2	2.02	20.20	4.49	7.51	12.63	5.00	3.67	6.52
Na_2O	1.07	0.32	0.15	8.38	1.90	7.56	0.52	10.07
K_2O								Trace.
Mn	Trace.	Trace.						
P							0.63	
H_2O	7.67	14.56	11.95	4.26	14.18	15.07	5.03	10.28
Organic matter [a]	2.98	5.50	3.10	3.67	0.20	0.05	1.42	2.85
$Ca_3(PO_4)_2$								1.07
Na_2CO_3								4.15
Clay								2.80
MgO	Trace.	Trace.	Trace.					

[a] Organic matter by difference.

EFFECT OF WATER CONTENT.

The first of the conditions studied was moisture content. One [3] of the authors of this paper, using a different method, had already studied the effect of moisture but the checking of his results by the rate-of-flow method herein described seemed advisable.

Water content as used in this paper includes all the water held by the oxide, regardless of the way in which it is held. The idea has prevailed among some chemists, and perhaps still prevails among a few, that water is held not only as surface moisture but in some materials also is combined with iron oxide to form hydrates of definite composition. This idea has been fostered by works on mineralogy that publish lists of hydrated iron oxides of definite chemical composition, which correspond to natural oxides of iron found in various localities. The list of hydrated iron oxides usually given is as follows:

Name.	Formula.	Percentage of water.
Turgite	$2Fe_2O_3 \cdot H_2O$	5.1
Goethite	$Fe_2O_3 \cdot H_2O$	10.1
Hydrogoethite	$3Fe_2O_3 \cdot 4H_2O$	13.0
Limonite	$2Fe_2O_3 \cdot 3H_2O$	14.5
Xanthosiderite	$Fe_2O_3 \cdot 2H_2O$	18.4
Limnite	$Fe_2O_3 \cdot 3H_2O$	25.3

It is well known that many oxides retain some of their water content with great tenacity, even when heated to a high temperature. This fact and the changes in appearance and structure of oxides after ignition has probably strengthened the opinion of some chemists

[3] Dunkley, Wm. A., Some conditions affecting the usefulness of iron oxide for city gas purification: Engineering Experiment Station, University of Illinois, Bull. 119, 1921. 62 pp.

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that hydrates of ferric oxide actually exist. Proof of their existence must rest, however, on both physical and chemical data. The latest work on ferric oxides that has come to the attention of the writers is that of Posnjak and Merwin[4] of the Geophysical Laboratory, who conclude, from some very careful physical-chemical work carried on for several months that no series of hydrates of ferric oxide exists among the natural minerals; that the one existing hydrate is the monohydrate ($Fe_2O_3.H_2O$); and that no definitely crystallized synthetic hydrates of ferric oxide have been prepared up to the present time. They feel certain that only two distinct types of "amorphous" hydrated ferric oxide exist—one yellow and the other reddish brown. The yellow is assumed to be essentially ferric oxide monohydrate, whereas the reddish-brown oxide may hold its water in either dissolved or adsorbed (not absorbed) condition or both. Thus the synthetic and the natural hydrated ferric oxides are chemically much alike.

While it does not seem, therefore, that any differences in the activity or other properties of oxides differing in water content can be attributed to the presence of hydrates of definite composition, still it has long been known that water content has, at least, an indirect bearing on the behavior of oxides. Ignited oxides or those that have been overheated during revivification are inactive to hydrogen sulphide and certain natural and artificial oxides that contain high percentages of water are exceptionally active. It seems reasonable, therefore, that differences in water content should explain certain differences in behavior.

ROSE-JANSCH METHOD OF DETERMINATION.

The study of the effects of water content upon activity necessarily involves two separate determinations for each activity figure obtained, namely, the water content and the maximum rate of gas flow possible with the described method.

For determining the water in each sample the Rose-Jansch method was used. A gram of the oxide was mixed with several times its weight of a previously dried mixture of litharge and lead peroxide. The charge was placed in a short tube of hard glass with a layer of dried lead peroxide, from which it was separated by a layer of ignited asbestos. The mixture was heated strongly with a Meker burner until it melted. During ignition a slow current of air, previously dried by passing through a calcium chloride tube, was passed over the charge. The water taken up by this air from the iron oxide was collected by another calcium chloride tube that had been weighed.

[4] Posnjak, Eugen, and Merwin, H. E., The hydrated ferric oxides: Am. Jour. Sci., vol. 47, 1919, pp. 311–358.

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The gain in weight of this tube during ignition gave the total weight of water in the sample of oxide.

A series of moisture-activity values for each oxide was obtained by drying in stages. The value was first determined for the sample as received. A portion was then set aside in a tightly stoppered bottle and the remainder was partly dried. A set of determinations of water content and activity was then made on a 1-gram portion of the sample, and a portion of the sample was dried further for another set of determinations. This process was repeated until a series of four or five points was obtained for each sample. Equal portions of another sample of the air-dried material were then moistened with different amounts of water and each sample was allowed to stand in a tightly stoppered glass bottle until the water had an opportunity to become thoroughly adsorbed by the oxide; then the activity of these portions was determined.

Figure 2 gives the results of the activity tests; the activity is expressed by the ordinates in cubic feet of gas flow per hour; the abscissas show the water content of the oxides. The curves bring out quite clearly the effect of water content on the behavior of oxides. Aside from the difference in activity of different oxides at the same water content, differences in water content affect the activity of the same oxide. Each oxide has a best water content at which it is most active. Increasing or decreasing the water content from this optimum decreases activity. Moreover, small variations of water content have less effect on the activity of some oxides than of others. The water content of some oxides can be varied over an extremely wide range without materially affecting the activity, whereas even a very small variation in the water content of other oxides greatly changes the activity.

Operators of gas plants have probably often observed marked differences in the behavior of certain oxides in their plants, depending on whether the oxides were put into the purifiers dry or wet. In some plants it is common practice to wet down an oxide thoroughly before putting it into the box. Such procedure might sometimes be beneficial, but if the oxide happened to be of the type of No. 3, 4, or 7, the chance of excessive wetting would be great. It is interesting to note that the deep red or black oxides seem to be more sensitive to water content than the brown or yellowish-brown oxides.

INFLUENCE OF OXIDE SURFACE.

Probably the effect of water is influenced primarily by the oxide surface. The light colored oxides usually have low specific gravity and high specific volume, which indicate great porosity and large surface exposed. Such oxides may have a high water content and

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yet look dry—probably because the water is held by adsorption and each minute particle of the oxide is distended like a damp sponge by the water held within it. When an oxide is dried, it loses water and the structure seems to contract, just as a sponge contracts when dried. The surface exposed seems less and the activity decreases.

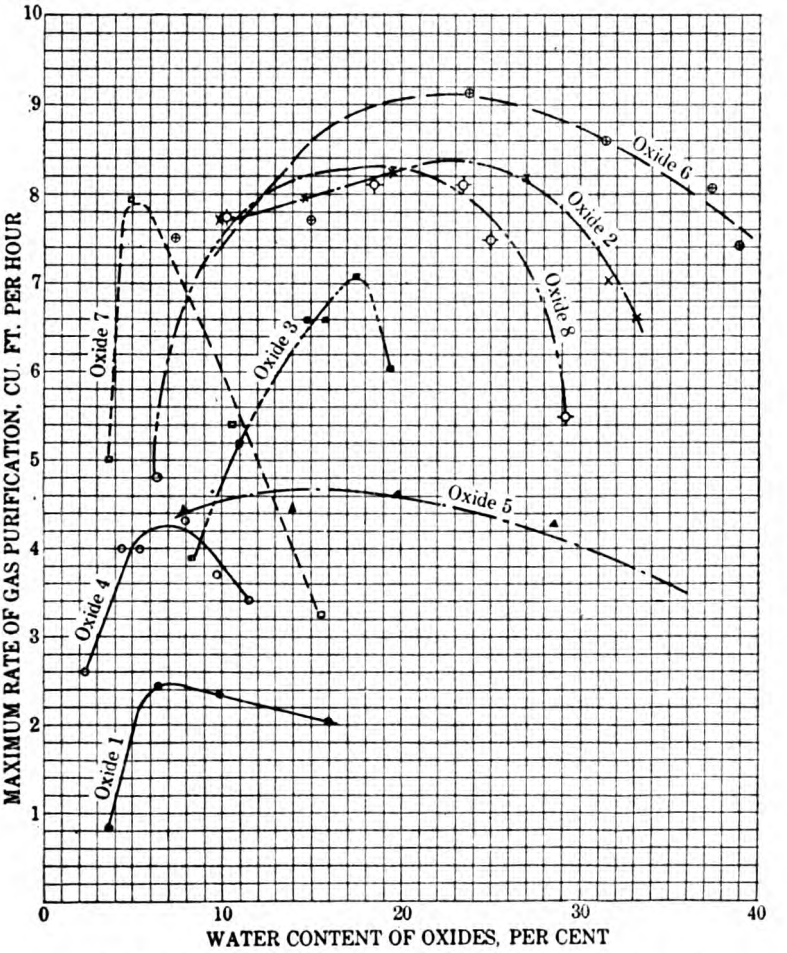

FIGURE 2.—Curves showing effect of water content on activity.

An oxide that has been ignited and has lost all of its contained water is practically inactive. On the other hand, excessive water seems to decrease activity by excluding the H_2S from contact with the oxide surfaces. Activity seems to be intimately connected with oxide surface. The surface oxide seems to react best with H_2S when damp, but excess water seems to fill all the pores of the oxide, "water log" it so to speak, and thus decrease its activity.

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Questions of interest to the gas operator are how may he be certain when his oxide has reached the proper moisture content and how may it be maintained in this condition. Even if it is assumed that laboratory tests will determine the best moisture content of an oxide, it is evident that the water content will vary after the oxide is put into use. If the gas is saturated with moisture as it enters the purifier and the temperature is reduced, water will be deposited in the oxide; if the gas enters comparatively dry, water will be removed from the oxide. Also the sulphiding reactions of gas purification have water as one of their products which shows that water is deposited in the oxide by the process. Regulation, therefore, seems difficult.

MOISTURE CONTENT IN PRACTICE.

Assistant Engineer H. R. Cook, of the Baltimore Consolidated Gas Co., has reported plant observations which throw some light on the effects of moisture content in practice. The introduction of steam to the boxes was tried in one plant and, for a time, the action of the oxide improved, but afterwards the activity began to decline. When steam was temporarily discontinued the oxide performance improved for a time and then declined. Repeating the use of steam gave the same results as before. In the light of the experimental results shown in Figure 2, the reason for this behavior is evident. The steam at first brought the oxide up to its most favorable water content and improved purification resulted. Further use of steam loaded the oxide with excessive moisture and purification declined. Operation without steam dried out the oxide and brought the activity again to the peak of its curve; further drying carried activity over the peak and results went down. This behavior of the purifying material suggests a method of operation.

If an operator can so dry his gas by cooling and condensation that when it reaches the purifier it is cooler than the purifying material, it will on warming become unsaturated with water vapor and will tend to remove water from the oxide. He can then introduce just enough steam, as determined by experiment, to keep the oxide at highest efficiency. Heating the purifiers by external heat or closed steam coils in the boxes will have a tendency to dry out the oxide and this drying may be excessive unless compensated by the introduction of steam.

Gas companies during many years have occasionally tried the use of steam in purifiers. Inquiry among the companies would probably call forth a wide variety of opinions on the efficiency of steam but reasons for variations in the success of the procedure have been pointed out in the foregoing discussion and it is probable that failures in the process may be attributed to too much or too little steam.

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EXPERIMENTAL METHOD OF DETERMINATION.

As the curves of Figure 2 are similar to those one of the authors [5] of this paper obtained by use of the one-minute fouling method with pure H_2S gas, the results on activity obtained by drying and remoistening an oxide sample by this method are given in Figure 3. In the original chart the H_2S absorption and water content were expressed as ratios to the Fe_2O_3 content of the oxides, but in Figure 3

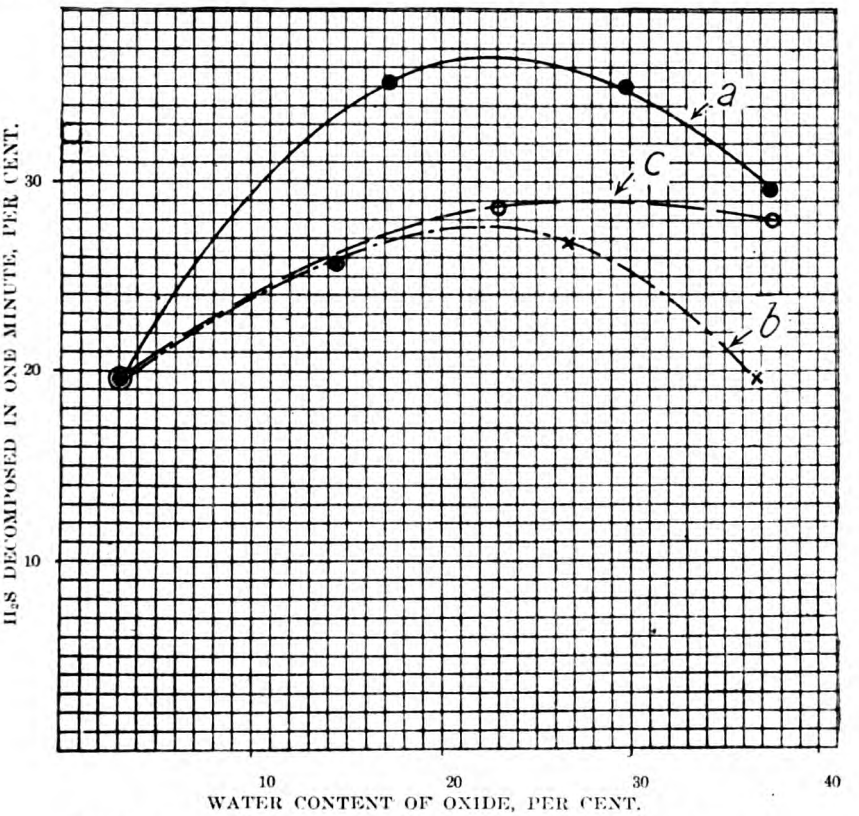

FIGURE 3.—Curves showing how drying and remoistening affect activity.

the Fe_2O_3 factor is omitted; the ordinates represent H_2S decomposed per minute and the abscissas represent simply water content. The sample of oxide represented by Figure 3 was dried in stages, and its moisture, iron oxide content, and activity were determined at each stage. The oxide had the highest water content when in the "as received" condition, and had lowest water content after drying two or three hours at 400° F. Curve *a* was obtained from this series of determinations.

[5] Dunkley, Wm. A., Some conditions affecting the usefulness of iron oxide for city gas purification: Engineering Experiment Station, University of Illinois, Bull. 119, 1921, p. 33.

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The dried sample was divided into portions and these portions were remoistened with different amounts of water. The Fe_2O_3 content, water content, and activity of each portion was determined as soon as the portions had been thoroughly stirred to incorporate the moisture. Between tests the samples were kept in tightly stoppered bottles. Curve *b* resulted from these tests, which were made as soon as possible after remoistening. Three days later portions of the same remoistened samples were again tested for activity, and the data shown by curve *c* were obtained.

These curves clearly show that a dried sample of oxide does not regain its activity immediately after remoistening and does not regain it completely even after contact with moisture for several days. Readsorption of moisture is a slow process and complete rehydration may be a matter of weeks or months. Indeed, there are indications that if an oxide be heated to a somewhat higher temperature than that used in the experiment, rehydration becomes much slower. A sample of oxide that had been heated for several hours at 750° F. failed to rehydrate to any apparent degree even after digestion with water in an autoclave at 200° C. for two or three days. This explains why oxide is sometimes ruined as a purifier by overheating during preparation or during revivification.

SULPHIDING AND REVIVIFICATION.

The question has often arisen whether oxide regains its previous water content after sulphiding and revivification. To answer this question an oxide, a yellowish-brown hydrated natural ore, was partly dehydrated by drying for several hours at 400° C. (752° F.). Its color changed to deep red. A 1-gram sample of the original oxide and a 1-gram sample of the partly dehydrated oxide were placed in an oven at 105° C. to expel any surface moisture that might be present. The water content of each sample was determined by the Rose-Jansch method already described. Two similarly dried samples were moistened slightly and sulphided; care was taken not to allow the temperatures to become excessive. The sulphides produced were moistened slightly and allowed to revivify slowly in air. Both samples revivified well and regained practically the colors they had before sulphiding—one yellowish brown and the other deep red. The revivified oxides were dried several hours at 105° C. and the water content then determined with the following results:

Water content of oxides.

	Hydrated oxide.	Dehydrated oxide.
Fe_2O_3 content (after drying at 105° C.), per cent	66.80	90.10
H_2O content (after drying at 105° C.), per cent	18.02	6.24
H_2O content (after sulphiding, revivifying, and drying at 105° C.), per cent	12.35	5.82
Ratio H_2O: Fe_2O_3 before fouling, per cent	27.0	6.9
Ratio H_2O: Fe_2O_3 after fouling, per cent	18.5	6.4

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The results indicate that an oxide fouled and revivified regains practically the same moisture content or a little less than it had before fouling. If the oxide has previously been overheated and dehydrated, even the chemical reactions of sulphiding and revivifying in the presence of excess moisture do not suffice to restore it to its original hydrated condition. It would seem that during these chemical reactions, the cycle from oxide to sulphide and back to oxide is accomplished with very little if any change in the physical structure unless exceptional heating or other external effects are brought to bear. This suggests the reason why some oxides revivify more rapidly than others. An oxide active in sulphiding is likely to be active in revivification because it retains throughout the sulphiding and the revivifying, if these are normally conducted, a surface structure that is conducive to rapid chemical action; retaining this structure, it also regains essentially the water content that the structures enables it to hold.

EFFECT OF TEMPERATURE.

The temperature of the oxide as affecting purification is another variable condition that has been much discussed. It is well known that heat promotes most chemical reactions. In gas purification the fact has been recognized from the beginning of the gas industry. The elaborate buildings erected to house purifiers in the earlier days of the gas industry attest to the general belief that warmth favors the purifying reactions. Of course, the fact that water seals on purifiers were then universal made the heating of the purifiers in cold weather a matter of some importance. The present practice of building purifiers outdoors indicates that experience has not justified large expenditures for housing and that a high enough temperature can be maintained by the heat of the gas itself and the temperature of the purifying reactions.

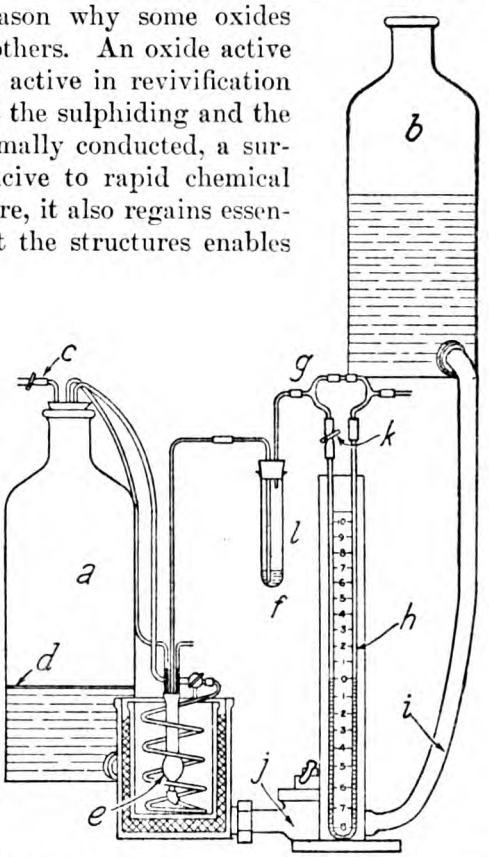

FIGURE 4.—Apparatus for determining effect of temperature on activity.

Figure 4 shows the apparatus as finally arranged for determining activity. A crude thermostat, which consisted of two earthen-

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ware jars set one within the other, the intervening space being packed with sawdust for insulation, was connected between the gas storage bottle *a* and the indicator tube *f*. The mixture of inert gas with H_2S from *a* passed downward through a spiral coil surrounding the reaction tube *e*, then through the tube *e*, which was packed as previously described, and then to the indicator tube *f*. In a test the reaction tube *e* was charged, connected to the glass coil, and lowered into the jar. Water at about test temperature was poured into the jar until the tube *e* and glass coil were submerged. They were allowed to stand for 15 minutes before testing. Experiment showed that in 15 minutes the oxide had practically the temperature of the bath.

Temperatures from about 45° F. to 150° F. were readily obtainable and seemed to give variation enough to cover the practical range. Since temperatures above that at which the oxides had been air dried would cause evaporation of water from the oxides and thereby change their water content, thus introducing that variable, it was decided to use samples of oxide that had been dried at 105° C. The moisture content of oxide thus prepared could not be decreased by the temperature of the bath. It was thought at first that the moisture content and activity might be altered by the humidity of the incoming gas from *a* and a calcium chloride tube was inserted to dry the gas mixture. Later, however, it was omitted because it only increased the volume of air to be swept out by the gas mixture and had no appreciable effect on the observed activity of the samples.

Only two oxides were tested for temperature effect. Of these No. 1 was a black by-product oxide and No. 2 was a natural oxide. Figure 5 indicates that temperatures within the commercial range have a relatively small effect on oxide activity, which increases from 45° F. up to about 120° F., and then declines slightly. To explain this decline is difficult. Had the oxide not been previously dried at a temperature higher than that of the test, this decrease might be attributed to the oxide losing water, but under the circumstances a loss of water by the oxide is hardly conceivable; and if water were gained from the gas, the tendency would be to increase rather than decrease the activity of the previously dried oxide.

The curves of Figure 5 indicate that the temperature of purification (around 100° F.), which has been generally regarded as favorable in practice, is not far from the most favorable temperature as shown by test. In practice the temperature carried at the purifiers may be governed largely by the necessities of tar removal, but the experiments described give no evidence that much higher temperatures would be favorable in practice even were the carrying of higher temperatures otherwise practical.

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The results of this experiment are partly corroborated by tests made by the 1920 Purification Committee of the American Gas

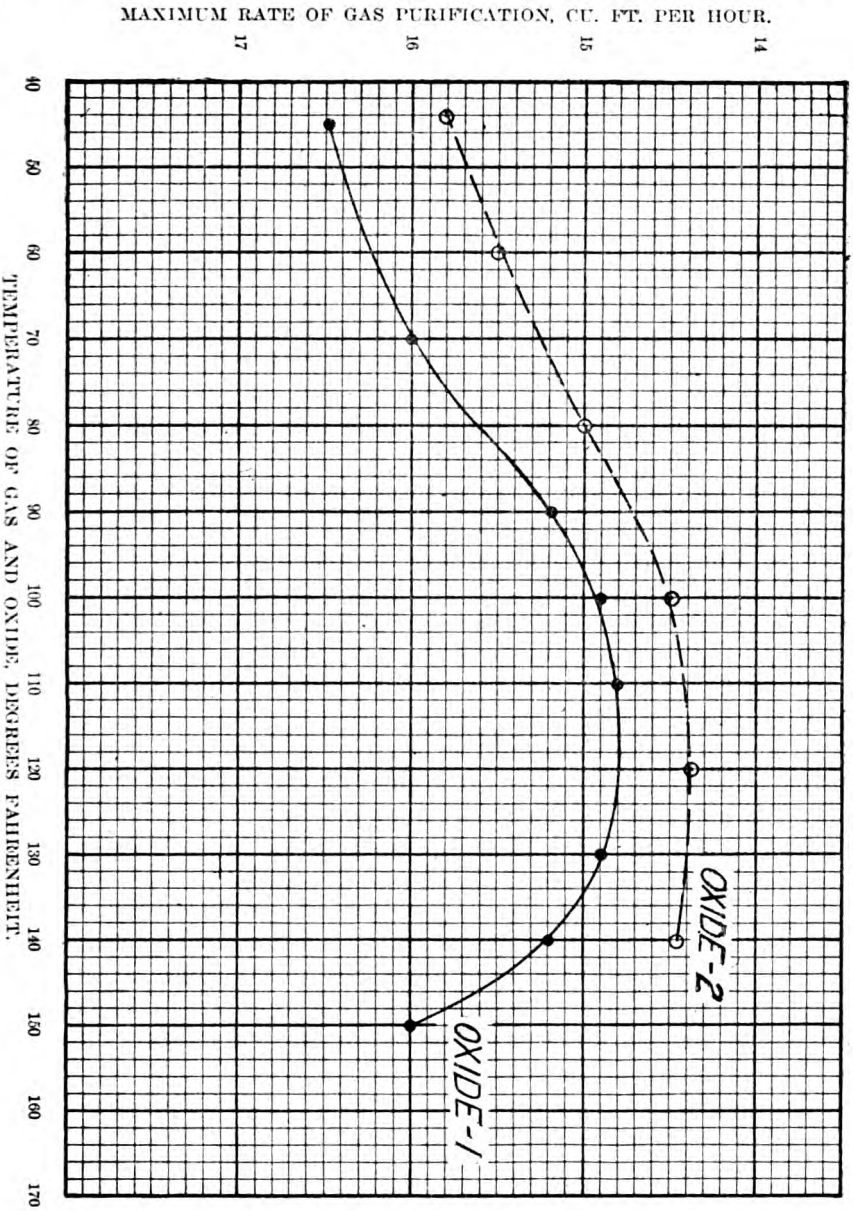

FIGURE 5.—Curves showing effect of temperature on activity.

Association.[6] It used a layer of oxide 9 inches deep in a piece of 4-inch pipe that could be immersed in a heating bath. Gas contain-

[6]Stone, C. H., Report of purification committee: Proc. Am. Gas. Assoc., Technical Section, 1920. 35 pp.

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ing 263 grains of H_2S per 100 cubic feet was passed into the oxide, and the H_2S content of the exit gas was determined. The efficiency of purification increased from 73 per cent at 60° F. to 87 per cent at 120° F., the highest temperature at which tests were made.

EFFECT OF HYDROGEN SULPHIDE CONCENTRATION.

Concentration of H_2S in the gas to be purified is another variable likely to affect the rate of the sulphiding reaction, and is one that has placed doubt on any test of oxides which involved the use of concentrated H_2S for fouling. In practice the H_2S concentration in gas is relatively low. A gas that contains 1 per cent of H_2S (about 600 grains per 100 cubic feet) is usually regarded as exceptionally high in sulphur. Coal gas from low-sulphur coals usually does contain more than 250 to 350 grains of H_2S at the inlet of the purifiers. Water gas from low-sulphur cokes or coals and low-sulphur oils do not usually contain more than 100 to 150 grains of H_2S at the inlet to the first purifier, in the gas-plant series; the subsequent purifiers handled more dilute mixtures. The last purifier may have only 10 grains or less of H_2S per 100 cubic feet to be removed from the gas, but this must be removed completely. When the oxide is fouled slowly with a low concentration of H_2S, the purifying reactions may differ from those that occur when the oxide is suddenly subjected to an excess of pure H_2S gas. The operator is interested mainly in the behavior of oxide within the range of purification practice.

Figure 6 shows the results of activity tests of a number of air-dried oxides, with H_2S concentrations from 10 grains to 1,000 grains per 100 cubic feet of gas. Owing to the fact, as previously determined, that 5 per cent lead acetate solution was not sufficiently sensitive with concentrations of H_2S below 200 grains per 100 cubic feet of gas, very dilute potassium permanganate solution was used as the indicator throughout the concentration tests. The use of this more sensitive indicator gives lower results, especially at low concentrations, than would be obtained with lead acetate, but as relative values rather than absolute values are sought in these determinations, this point is of no consequence.

Inspection of Figure 6 shows that the activities of all the samples tested were greater with very low concentrations than with somewhat higher concentrations. Also, the activities of all the oxides were nearly equal with the very low concentrations but the activity curves fall and diverge as the concentrations increased. The tendency of several of the activity curves to converge again at the high concentrations is of interest. Nearly all of the oxides seemed to pass through a minimum point at some intermediate concentration and then rise slightly with increasing concentration. A certain de-

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gree of experimental error unavoidably enters into a method of this kind and it is possible that the activities are really constant with the higher concentrations, though the tendency to increase activity is perceptible in every test but one.

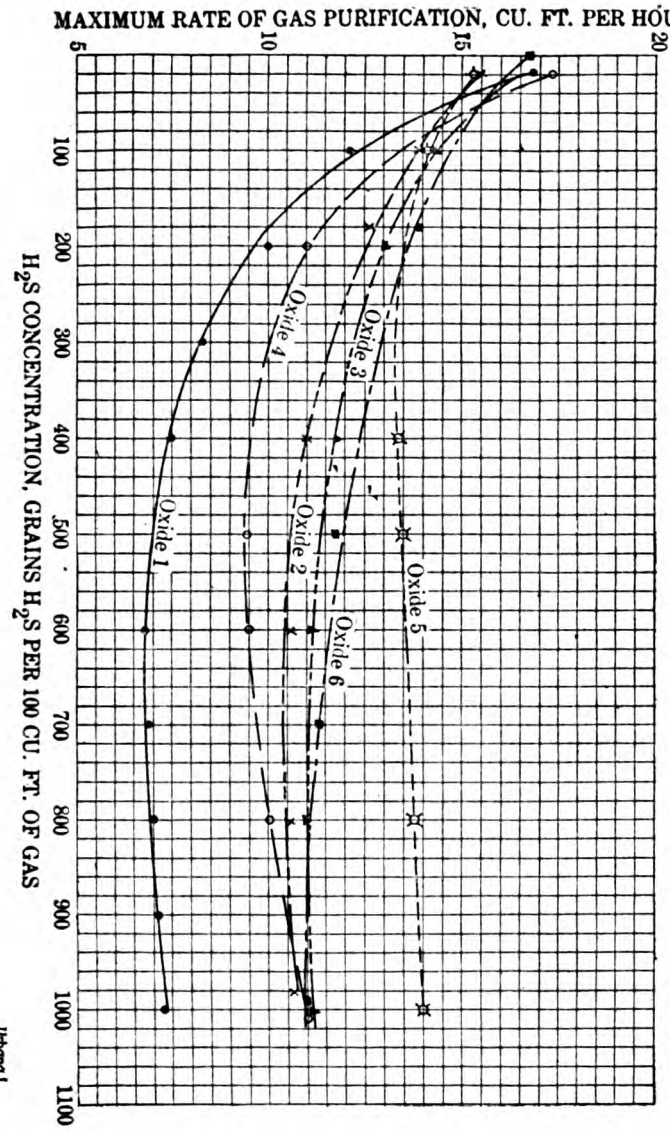

FIGURE 6.—Curves showing how hydrogen sulphide concentration affects activity.

With very low concentrations such as 20 grains or less of H_2S per 100 cubic feet, it is difficult to obtain the necessary rate of gas flow because of the resistance to the flow of water and gas through the apparatus. There is consequently some likelihood of error in the activity figures at these low concentrations. It would be natural

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to expect very sharp rises in all the curves at zero concentration of H_2S because the activity with no H_2S would be infinite; but with even a trace of H_2S present the element of time of reaction begins to affect the activity. It is evident, therefore, that the curves can not proceed entirely to the zero concentration line in the direction indicated.

Absorption may possibly have some effect on the observed results; the oxides may have the property of taking up physically a portion of the H_2S before the chemical reaction really gets under way. Adsorption of certain gases by activated charcoal in Army gas masks is a similar action. With low concentrations of H_2S, a considerable portion of the sulphur is possibly removed in this way, allowing only traces to pass at high rates of flow. At higher concentrations, it seems probable that the amounts of H_2S taken up by adsorption are at least as great as with low concentrations, but these amounts represent a much smaller percentage of the total H_2S passing into the oxide at a given rate of gas flow; hence the amount absorbed is not sufficient to prevent traces of H_2S from passing the oxide of rates of flow lower than those when the concentration was lower.

From the curves of Figure 6 it is evident that the activity of an oxide is not inversely proportional to the concentration of H_2S in the gas coming to it. With increasing H_2S content in the gas, the activity decreases to a certain point after which it remains almost constant. Therefore although gas of very low sulphur content can be purified at a comparatively high rate due to adsorption, gases with higher concentrations of H_2S can be purified at very nearly a constant rate regardless of their sulphur content.

This statement applies, of course, only to new oxides and their initial activity. The effect of H_2S concentration upon oxide performance under actual operating conditions, where the purifiers receive gas of a certain H_2S content over a protracted period, is somewhat different. As the exposure to the action of H_2S is long continued, the content of active oxide in the purifying material is, of course, changing. The effect of H_2S concentration on oxide behavior under practical operating conditions has been deduced by the Steere Engineering Co.[7] from a study of numerous purifying installations. The company deduces a formula showing the maximum amount of gas in cubic feet per hour that can be purified by a given installation as follows:

$$\text{Purifier capacity} = \frac{3000 \times (D+C) \times A}{S}$$

Where D=total depth, in feet, of oxide through which the gas passes consecutively in the purifier set; C=factor, 2 for two-box,

[7] Steere, F. W., Principles of gas purification and purifier design: Gas Age, vol. 43, 1919, pp. 227–231.

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8 for three-box, and 10 for four-box series, respectively. Where a single catch-box is used for two-box sets, use factor $C=6$; A=cross sectional area, in square feet, of the oxide through which the gas passes on its way through any one-box, in the series. The quantity S is dependent on the H_2S content of the gas, but is not directly proportional to it. The following values of this factor are given for various H_2S contents:

Grains H_2S per 100 cubic feet:	Value of S.	Grains H_2S per 100 cubic feet:	Value of S.
1,000 or more	720	500	560
900	700	400	525
800	675	300	500
700	640	200 or less	480
600	600		

If these values of S are substituted successively in the formula for purifier capacity and values be assigned D, C, and A that will give a capacity of 100,000 cubic feet of gas purified per hour when the value of S is 480, corresponding to 200 grains (or less) of H_2S per 100 cubic feet, then the purifying capacities corresponding to various H_2S concentrations are shown by the full-line curve of Figure 7. It will be noted that this curve is not simple; the value corresponding to 600 grains of H_2S per 100 cubic feet lies in the middle of a straight line between two curves. The nature of the relation would not lead one to expect a curve of this form had the values been deduced from the results of experiments.

The Steere formula, however, is for use in the practical designing of purifying equipment and consequently must take into account a proper factor of safety. Accordingly, the values of S corresponding to H_2S concentrations less than 600 grains per 100 cubic feet have been made larger than they should be in proportion to the value corresponding to 600 grains. On the other hand, with concentrations above 600 grains the values of S have been made smaller than in proportion to the value of S for 600 grains. Seemingly, this change recognizes the condition indicated in Figure 6—that the rate at which an oxide can purify gas decreases very slowly (if at all) when the H_2S concentration increases beyond 600 grains per 100 cubic feet. This condition, of course, is true only within limits, for an oxide is fouled more rapidly by a gas containing 1,000 grains of H_2S per 100 cubic feet than by gas containing 500 grains of H_2S per 100 cubic feet. It seems likely that the relation shown in Figure 7 would follow more nearly the dotted extension, for H_2S concentrations below 600, if no allowance for factor of safety were made. With such a modification, the curve takes the same general form as the curves of Figure 6. The Steere formula takes no account of differences in oxides, but the effects of H_2S concentration as deduced by the authors of this paper are observed in works practice.

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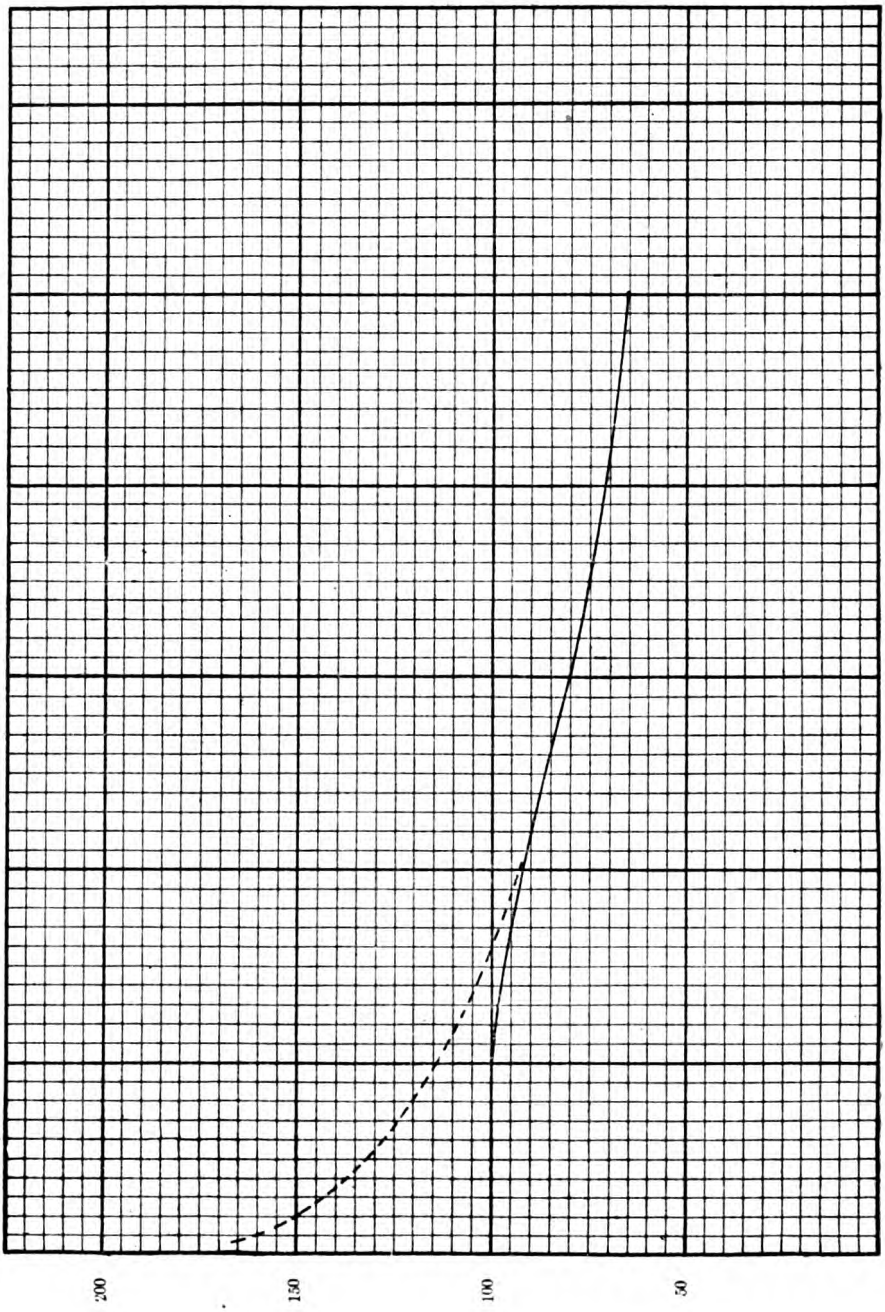
MAXIMUM HOURLY PURIFYING RATE—1,000 CU. FT. PER HOUR.



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EFFECT OF PARTIAL SULPHIDING ON ACTIVITY.

An oxide begins to lose its activity as soon as it is put into use; its sulphur content is cumulative. As more and more H_2S is decomposed, the amount of active oxide is decreased by transformation into sulphide. If, as observation seems to indicate, the activity of an oxide depends on the extent of active surface exposed, it seems likely that the first sulphiding on exposure to H_2S is mainly superficial. After the surface is sulphided, the sulphiding reaction penetrates more deeply. In an active oxide, so dispersed that a comparatively large part of the mass is at or near the surface, the sulphiding action will presumably be much more rapid than in one that is more dense and compact.

A question of interest is whether an oxide that is more rapid in action when fresh retains this activity after being partly sulphided, or is then likely to lose it more quickly. To determine this point, several oxides were fouled to different degrees with pure H_2S by the Kunberger method, in which the weight of H_2S decomposed is determined by the gain in weight of the fouled sample, and any water formed by the reaction is retained by a calcium chloride tube connected to and weighed with the oxide tube. In the tests the oxide tube was packed for the rate-of-flow method described on page 6. After partial fouling, the tube was kept tightly corked until after it was weighed and its activity was determined immediately by the rate-of-flow method. The curves of Figure 8 show the results obtained.

It is interesting to note that many of the oxides showing the high initial activity lose their activity rapidly—in fact, some of the curves cross. On the other hand, certain oxides of considerable lower initial activity maintain activity even after a high percentage of fouling. In Figure 8, curves 5 and 3 are of interest. Oxide 5, a by-product precipitated oxide, was a light yellow brown. As it had a low specific gravity, its exposed surface was probably large. Oxide 3 was a rust oxide. Although the activity of oxide 5 was far greater at the start, it decreased very rapidly as fouling progressed, and at about 37 per cent fouling fell below that of No. 3 at the same degree of fouling. The activity of oxide 5 continued to decline rapidly, whereas that of No. 3 remained almost constant until fouling exceeded 80 per cent. A logical inference from these curves is that if an oxide is used without any revivification in place, its initial activity is necessarily an indication of the activity throughout the period of use.

If, as in many plants, a part of the revivification takes place in the purifiers, another factor must be considered, namely, the rate of revivification. This point the writers have not studied as yet.

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Since the rate of revivification, like the rate of sulphiding, probably depends on the superficial area of the material, it seems likely that an oxide which sulphides rapidly will also revivify rapidly. If that is true, it would seem that under favorable conditions of flow reversal and purifier rotation a rapid oxide might revivify so quickly that it might have throughout the greater part of its active life a higher average activity than an initially less active material.

If the action of oxide 3 is typical of the class of oxides made by the rusting of iron borings, it may explain why many operators of small gas plants without facilities for revivifying oxides in place have found that, under their operating conditions, the rust oxides

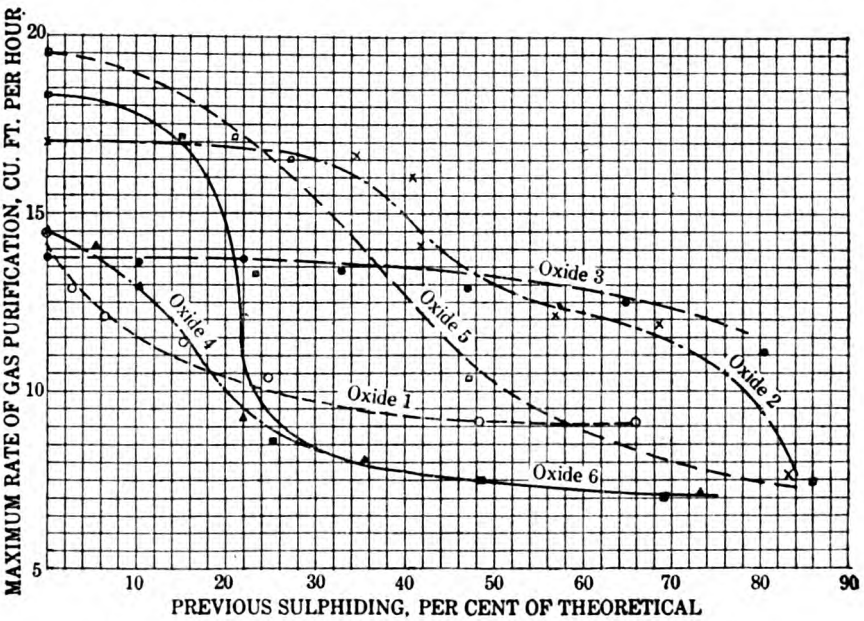

FIGURE 8.—Curves showing effect of partial sulphiding on activity.

give generally satisfactory service, and therefore have continued to be used year after year.

The curves of Figure 8 do much toward demonstrating the hypothesis that the determined activity of a fresh material does not by itself suffice for judging the ultimate value of the material for gas purification under all conditions. As previously suggested, initial activity may prove to be a measure of value where conditions are favorable for revivification of oxide in the box; where they are not favorable, initial activity is a poor indicator of ultimate value.

EFFECT OF TAR UPON OXIDE PERFORMANCE.

One of the worst of all the conditions hindering the realization of the full purifying value of an oxide in practice is the presence of tar

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in the gas. An oxide purifier serving as a tar extractor represents waste. The oxide removes the tar thoroughly, but using it for that purpose is very expensive. An operator does not intend, of course, to use his purifiers as tar extractors, but it is unfortunately true that the gas-cleaning capacity of a very large percentage of the plants in the United States is inadequate, and more or less tar inevitably reaches the oxide purifiers.

One of the authors of this paper made a survey of purifier conditions in the medium-size gas plants in Illinois [8] and found that tar was present in the gas entering the purifiers in 15 out of 16 plants in which tests were made. Half of the plants inspected produced water gas and the other half produced mixed coal and water gas. In some of the plants, especially those in which all or a large part of the gas was water gas, the amount of tar carried into the purifiers was very great. In one water-gas plant the test indicated that as much as 250 pounds of tar was carried into the purifiers with each million cubic feet of gas purified. Under such conditions the purifying value of an oxide would be quickly ruined. Although conditions in the average plant are doubtless much better than this, still it is probably true that more oxide is prematurely ruined by tar than is actually spent by the sulphur deposited within it. As the activity of oxides in purifying gas probably is governed largely by the extent of oxide surface exposed to the H_2S in the gas, a probable explanation of the deleterious effect of tar is that a tar film deposited on the surface of the oxide fills the interstices between the oxide particles and thus excludes the gas.

In order to obtain some measure of the effect of tar on oxide activity, the authors carried out an experiment in which an attempt was made to duplicate the effects of tar deposition in gas-purifying practice. A weighed amount of water-gas tar was dissolved in pure carbon disulphide. The solution was made up to a definite volume by the addition of more carbon disulphide, and measured volumes of the solution were added to weighed samples of an oxide in such proportions that the samples contained 5, 10, 15, and 20 per cent of tar. Each sample of oxide was thoroughly mixed with the solution and set in a warm place where a current of air was passed over it until the carbon disulphide completely evaporated leaving the tar deposited on the oxide. Even the sample treated with 20 per cent of its weight of tar was not sticky after drying and its particles did not cohere much. The color was somewhat darker than that of the untreated oxide. Portions of all the samples were then subjected to the rate-of-flow activity test.

[8] Dunkley, W. A., and Barnes, C. E., Gas purification in the medium-size gas plants of Illinois: Illinois State Geol. Survey, Cooperating Mining Series, Bull. 25, 1920, 71 pp.

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Figure 9 shows that the activity of the oxide decreased as the percentage of the tar adsorbed increased. Addition of 20 per cent of tar decreased the activity about 18.5 per cent. Unfortunately, much of this decreased activity of oxide through the deposition of tar is

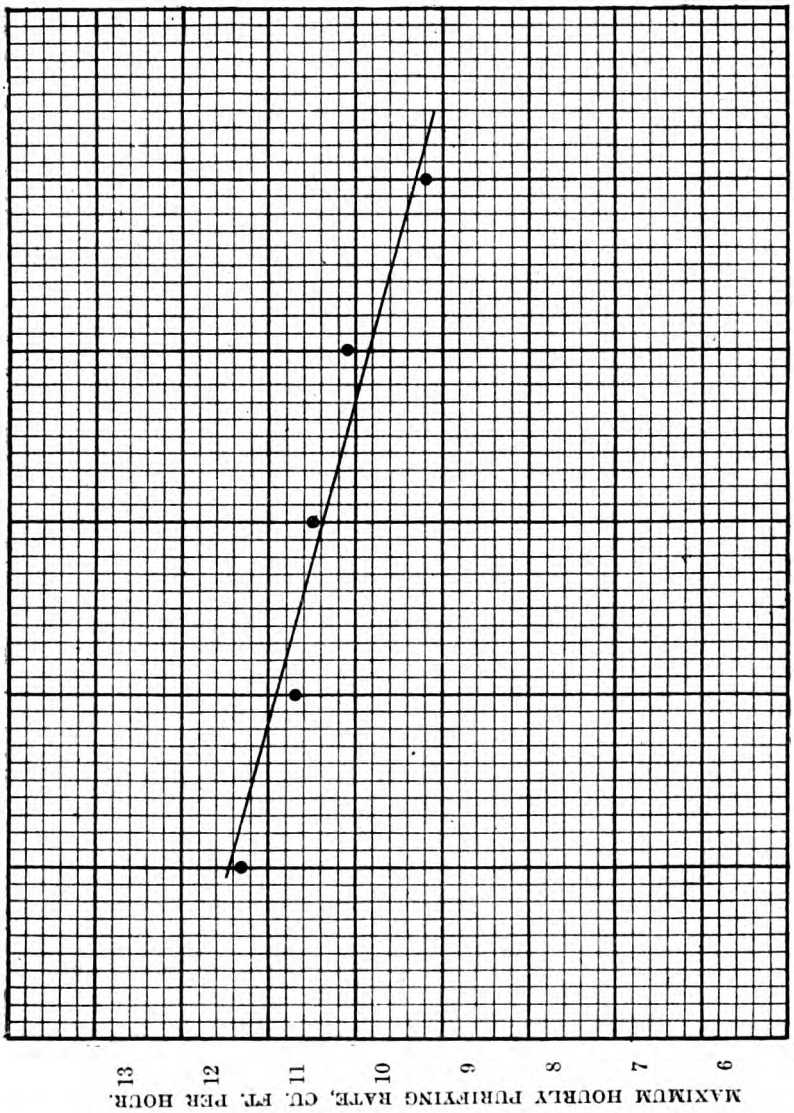

FIGURE 9.—Curve showing effect of tar on activity.

probably permanent, although exposure to outdoor air may improve a tarred oxide slightly. In the medium-size gas plants in Illinois inspected by one of the authors, the average tar content of the spent oxide ranged from about 3 per cent to about 25 per cent of the weight of the iron oxide present. In practice the deposition of tar

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is, of course, gradual. All the harmful effect is not experienced immediately, but the net result as shown by the inspection of the Illinois plants is that the active life of the oxide is reduced about 50 per cent. It is usually said that spent oxide should contain 50 to 60 per cent of its weight as free sulphur. Analyses of spent oxides from the plants inspected showed an average of about 25 per cent of sulphur in the spent oxide from water-gas plants, and 35 per cent of sulphur in the spent oxide from mixed-gas plants.

EFFECTS OF ACIDITY AND ALKALINITY OF OXIDE.

Operators of gas plants, especially the smaller plants, for many years have added lime to iron oxide to correct acidity and improve purification. It would seem that practice which involves considerable trouble and expense would not survive unless the results obtained were favorable.

A few experiments under controlled conditions have been made with a view to determining just what advantages were derived from the use of lime. The 1920 Purification Committee[9] of the American Gas Association conducted some tests of this kind in experimental purifier boxes. All the results obtained were not conclusive but the indications were that alkalinity increases the efficiency of many oxides and that an alkalinity of about 2 per cent (figured as $CaCO_3$) gives the best results.

C. H. Stone,[9] chairman of the committee, in his report says that the presence of lime has been of material benefit, not so much by increasing the total absorptive power as by increasing the activity. He also says that in one of the plants operated by his company, the liming of the oxide with hydrated lime enabled the plant to remove completely the last traces of H_2S, whereas without lime complete removal was impossible. Here is further evidence of the effect of lime on activity. One of the writers of this paper has obtained similar results by adding small amounts of soda. He found that adding a solution of commercial sal soda to a natural oxide (1 pound of the soda to 1 bushel of the sponge, the latter containing about 25 pounds of oxide) greatly increased the ability of the soda to remove on a plant-operation scale the last traces of H_2S from water gas.

In view of these results, the writer of this paper made some laboratory experiments to ascertain whether acids and alkalies materially affected the activity of oxides as determined in the experiments thus far described. In the first experiments, different volumes of dilute sulphuric acid were added to equal portions of the same oxide.

[9] Stone, C. H., Report of Purification Committee: Proc. Tech. Section, American Gas Assoc., 1920, 35 pp.

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After the acid solution had been thoroughly stirred in, the samples were dried for several hours in order that they might have as nearly as possible the same water content. Portions were then tested for activity. Results showed that the addition of sulphuric acid up to 10 per cent of the weight of the oxide had little effect on activity. In fact, addition of the acid seemed to increase activity slightly rather than to decrease it.

A probable explanation for this behavior is that the sulphuric acid itself had no effect on the activity but by its ability to hold moisture it enabled the oxide to retain more moisture at the temperature of drying than the latter could have retained by itself, and the small increase of activity was most likely due to their increase of moisture content.

Similarly, portions of oxide were treated with various amounts of sodium carbonate solution and allowed to dry several days. Under the conditions of this experiment the soda had no appreciable effect on activity. Finely powdered pure calcium carbonate was mixed dry with oxide and tested. Here again no effect whatever was discernible.

The results of these experiments seem to contradict the results obtained in practice and in the small test purifiers (p. 16), but the contradiction may be explained by the difference in methods of testing. In all of the reported results wherein the addition of alkali helped purification, air was admitted to the gas to assist revivification. It seems likely that as a consequence of the presence of air, secondary reactions take place in the purifiers and cause the formation of small amounts of sulphuric and sulphocyanic acids. Gedel[10] has shown that if acids are present in the oxide the action of H_2S (Fe_2O_3) results in the production of ferrous sulphide, free sulphur, and (under certain conditions) water; and at the temperatures that may exist at times in purifiers, the FeS and S may unite to form FeS_2 which does not revivify. On the other hand, if alkali is present in the oxide, H_2S and Fe_2O_3 combine to form Fe_2S_3 and water. Fe_2S_3 revivifies rapidly and does not combine with free sulphur to form ferric sulphide at these temperatures. Hence in the presence of air, as in the cases cited, and with alkali present the chief product of reaction was probably Fe_2S_3, much of which immediately revivified, thereby maintaining the activity of the oxide; whereas when no alkali was present, the more slowly revivified FeS was perhaps formed, resulting in a more rapid deterioration of the oxide. In the laboratory experiments for determining activity no air was present, and hence there was no opportunity for the effects of

[10] Gedel, Louis, Studies of iron sulphide with special reference to the purification of illuminating gas from H_2S. Thesis, translated by C. H. Stone and abstracted by A. R. Powell, Am. Gas Assoc. Monthly, September, 1922.

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alkalinity to become manifest. As has been said, the laboratory test indicates the initial activity of the oxide and is inherently incapable of showing how activity is affected subsequently by various conditions.

EFFECTS OF PROMOTERS ON ACTIVITY.

The time available for this investigation did not permit a study of the effects of promoters or catalyzers on the sulphiding reaction. This field seems attractive because, as has been frequently observed, many purifying materials that have a high content of iron oxide are very slow in reacting. If an inexpensive agent could be found which would promote the activity of those oxides, a highly satisfactory purifying agent might be developed. Cost must be considered and any such promoting agent would have to be marked at a moderate price and would have to be durable under gas-plant conditions. It is well known that catalytic agents employed in other processes can be "poisoned" by certain compounds such as carbon monoxide, cyanogen, etc.; consequently gas-purification conditions would probably be unfavorable for many agents that are good catalyzers for other processes.

The effects of water and of alkalies upon activity would probably be classed as catalytic by certain chemists. Indeed some chemists are disposed to class as a catalyzer the iron oxide used for purifying gas, because it brings about the oxidation of hydrogen sulphide to free sulphur and theoretically can be regenerated to its original condition.

SUMMARY OF CONCLUSIONS.

1. The activity of iron oxides for H_2S is affected by water content. Each oxide has a best water content or range of water content. Increasing or decreasing the water content beyond this range decreases activity.

2. The activity of some oxides is confined to a very narrow range of water content, but the activity of other oxides may continue almost constant while their moisture content increases several hundred per cent.

3. The activity of dark red or black oxides is usually more sensitive to changes in water content than is the activity of the yellow or yellowish-brown oxides. The latter oxides are usually of lower specific gravity and retain more moisture when apparently dry.

4. An oxide that has been dried and then remoistened does not immediately regain the activity corresponding to its water content. Complete readsorption may require several days or weeks. If the oxide is dried at temperatures of 400° C. it readsorbs water even more slowly.

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5. A thoroughly hydrated oxide that has sulphided and then revivified in the presence of plenty of water tends to resume the state of hydration which it had prior to sulphiding. A dehydrated oxide similarly treated tends to resume the dehydrated state even in the presence of excess water. From this it seems that throughout the sulphiding and revivifying process an oxide retains essentially the same physical structure.

6. The activity of oxides increases with increasing temperature to about 120° F.; above that temperature some oxides show only a slight decrease of activity, others show more. In the authors' experiments the total change in activity between 40° and 120° F. amounted to about 10 per cent.

7. At very low H_2S concentrations, all the oxides tested showed nearly the same activity. With increasing H_2S concentrations the activities of all oxides decreased, though the decrease for some oxides was slight. Some oxides showed a minimum activity with concentrations of about 500 to 700 grains of H_2S per 100 cubic feet of gas and a slightly increased activity with increased concentrations of H_2S. Other oxides attained an almost constant activity with H_2S concentrations varying from 600 grains per 100 cubic feet to 1,000 grains, the highest concentration tried.

8. The relation between activity of oxide and H_2S concentration as determined from the laboratory test appears to be essentially the same as the relation between concentration and purification rate by the Steere formula for purifier design.

9. Most oxides that show high activity when fresh do not maintain this superiority when partly fouled. Of the oxides tested, one produced by rusting cast-iron borings maintained the most uniform activity, losing only 14.5 per cent of its activity when sulphided up to 80 per cent. With the same degree of sulphiding, the activity of the oxide that initially was most rapid in action decreased 62.5 per cent.

10. In all tests of the activity of oxides the gas contained no air. Had the gas contained air those oxides that were initially more rapid might have revivified more quickly and have maintained a higher average activity.

11. Tar, if present, decreases the activity of the oxide, apparently by decreasing the oxide surface exposed to the H_2S in the gas. In the writer's experiments the percentage of decrease in activity was approximately proportional to the percentage of tar present in the oxide.

12. So far as could be ascertained, the presence of acid or alkali in an oxide has little effect on the initial activity of the oxide in the absence of air, except as it affects the capacity of the oxide to retain moisture at any given temperature. Experiments with miniature

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purifiers and tests during practical operation seem to show that alkalinity is of definite advantage in improving activity, apparently because it promotes the formation of the more easily revivified sulphide of iron, Fe_2S_3.

13. Sufficient time was not available for a study of the effects of various promoters on the purifying reactions except in so far as water and alkalies may be regarded as promoters.

14. Although the work described in this paper has demonstrated the effects of certain conditions on oxide activity, the authors do not claim that their method will definitely indicate the ultimate value of a fresh sample of an unknown material. Activity is changeable and is affected by many conditions. The method can be used, however, to compare the activity of one material with the activity of another at the time of testing. It seems likely, also, that the method is well suited for determining the purifying value of an oxide at different stages of its active life.

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